(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
7 December 2000 (07.12.2000)

PCT

(10) International Publication Number
WO 00/73356 A1

(51) International Patent Classification[7]: C08F 4/654, 10/02

(21) International Application Number: PCT/KR99/00639

(22) International Filing Date: 23 October 1999 (23.10.1999)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1999/19192 27 May 1999 (27.05.1999) KR

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(81) Designated States *(national)*: AT, BR, CA, CH, CN, DE, DK, ES, FI, GB, ID, IN, JP, LU, PT, SE, US.

(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *With international search report.*

WO 00/73356 A1

(54) Title: A CATALYST FOR ETHYLENE HOMO- AND CO-POLYMERIZATION

(57) Abstract: The present invention relates to a catalyst for homo-polymerization or co-polymerization of ethylene, or more particularly to a solid complex titanium catalyst for homo-polymerization or co-polymerization of ethylene, said catalyst being produced by preparing a magnesium solution by contact-reacting a halogenated magnesium compound with alcohol, reacting said solution with an ester compound having at least one hydroxy group and a silicon compound having an alkoxy group, and then reacting said solution with a mixture of a titanium compound and a silicon compound. The catalyst of the present invention has high activity with superior hydrogen sensitivity.

A CATALYST FOR ETHYLENE HOMO- AND CO-POLYMERIZATION

Technical Field

The present invention relates to a catalyst for homo-polymerization or co-polymerization of ethylene, or more particularly to a high-activity titanium solid complex catalyst supported in a carrier containing magnesium, said catalyst showing high catalytic activity, high bulk density, and high hydrogen sensitivity.

Background of the Invention

Catalysts containing magnesium for polymerization or co-polymerization of ethylene are known to have very high catalytic activities and to accord good bulk density, which are in turn suitable for liquid phase or gas phase polymerization. By liquid phase polymerization of ethylene, it denotes the polymerization process performed in such medium of bulk ethylene, isopentane, or hexane, and as for the important characteristics in consideration of the applicability of the catalyst used in this process, they are as follows: high activity, bulk density, the amount of molecules of low molecular weight dissolved in a medium, etc. Furthermore, in most of these manufacturing processes, hydrogen is used to control the molecular weight. The changes in the molecular weight (hereinafter hydrogen sensitivity) according to the amount of hydrogen is another characteristic of a catalyst, which is different per catalyst. The catalyst with high hydrogen sensitivity can control the molecular weight by using less amount of hydrogen at the time of the application of the process. As such, it provides more leeway with respect to the operation of the process.

Many of the titanium-based catalysts containing magnesium for olefin polymerization, and the manufacturing methods thereof have been reported. Especially, many processes making use of magnesium solutions to obtain olefin polymerization catalysts of good bulk density have been known. There is a means of obtaining a magnesium solution by reacting magnesium compounds with such electron donors as alcohol, amine, cyclic ether, or organic carboxylic acid in the presence of a hydrocarbon solvent. As for the cases of use of alcohol, they are disclosed in US Patent Nos. 4,330,649, and 5,106,807. Further, the methods for production of catalysts containing magnesium by reacting a liquid magnesium solution with a halogenated compound such as titanium tetrachloride are well known. Such catalysts provide good bulk density, but

there is much yet to be improved with respect to their catalytic activities and hydrogen sensitivity. In US Patent Nos. 4,477,639 and 4,518,706, a cyclic ether, tetrahydrofurane was used as a solvent of the magnesium compound.

US Patent Nos. 4,847,227, 4,816,433, 4,829,037, 4,970,186, and 5,130,284 claimed the methods of producing olefin polymerization catalysts of good bulk density, with superior polymerization activity due to the reaction of a titanium chloride compound with an electron donor compound such as magnesium alkoxide, dialkyl phthalate, and phthaloyl chloride.

US Patent No. 5,459,116 reports the method of producing supported titanium solid catalysts by means of contact-reacting a titanium compound and a magnesium solution containing an ester having at least one hydroxy group as an electron donor. By using this method, it is possible to obtain a catalyst of superior polymerization activity and bulk density. However, there remain things to be improved with respect to hydrogen sensitivity.

US Patent No. 5,869,418 shows the method of increasing hydrogen sensitivity by using a dialkoxyphenylalkane in the propylene polymerization as an external electron donor, and the advantages of such method. However, the above effects were obtained by using the external electron donor in addition to the solid catalyst, and also it is limited to polymerization and co-polymerization of propylene.

Summary of the Invention

As shown above, there is a need for the development of a new catalyst for homo-polymerization and co-polymerization of ethylene for producing polymers with the following conditions: simple manufacturing process, high polymerization activity, high bulk density for polymers by means of controlling the catalyst particles, and high hydrogen sensitivity. In the present invention, therefore, it is intended to provide a method for producing, from low-cost compounds via a simple process, a catalyst having an excellent catalytic activity and superior hydrogen sensitivity, capable of producing polymers of good bulk density. Further, the specific production process of catalysts and the steps thereof as disclosed in the present invention have never been reported in the prior art.

Consequently, the objective of the present invention is to provide a new catalyst solid component for homo-polymerization or co-polymerization of ethylene, said catalyst having

superior catalytic activity and hydrogen sensitivity, capable of producing polymers of high bulk density. More specifically, the objective of the present invention lies in providing a catalyst solid component for homo-polymerization or co-polymerization of ethylene, having a superior hydrogen sensitivity, wherein the form of the catalyst particles are controlled therein.

Another objective of the present invention is to provide a simple process for producing a catalyst for homo-polymerization or co-polymerization of ethylene.

Still other objectives and the advantages of the present invention will become apparent as references are made with respect to the following descriptions and the claims thereto.

Detailed Description of the Preferred Embodiments

The catalyst of superior catalytic activity and hydrogen sensitivity, capable of producing polymers having high bulk density as provided in the present invention, is produced by a simple yet efficient manufacturing process, which comprises (i) preparing a magnesium solution by contact-reacting a halogenated magnesium compound with an alcohol, (ii) reacting the same with an ester compound containing at least one hydroxy group and a silicon compound containing an alkoxy group, and (iii) producing a solid titanium catalyst by adding a mixture of a titanium compound and a silicon compound.

Types of halogenated magnesium compounds used in the present invention are as follows: di-halogenated magnesiums such as magnesium chloride, magnesium iodide, magnesium fluoride, and magnesium bromide; alkymagnesium halides such as methylmagnesium halide, ethylmagnesium halide, propylmagnesium halide, butylmagnesium halide, isobutylmagnesium halide, hexylmagnesium halide, amylmagnesium halide; alkoxymagnesium halides such as methoxymagnesium halide, ethoxymagnesium halide, isopropoxymagnesium halide, butoxymagnesium halide, octoxymagnesium halide; and aryloxymagnesium halides such as phenoxymagnesium halide and methyl-phenoxymagnesium halide. Of the above magnesium compounds, two or more compounds can be used in a mixture. Further, the above magnesium compounds can be effectively used in the form of a complex compound with other metals.

Of the compounds listed above, some can be represented by a simple formula, but the others cannot be so represented depending on the production methods of magnesium compounds. In the latter cases, it can be generally regarded as a mixture of some of the listed compounds. For example, the following compounds can be used in the present invention: such compounds obtained by reacting magnesium compounds with polysilolxane compounds, silane compounds containing halogen, ester, or alcohol; and such compounds obtained by reacting magnesium metals with alcohol, phenol, or ether in the presence of halosilane, phosphorus pentachloride, or thionyl chloride. However, the preferable magnesium compounds are magnesium halides, especially magnesium chloride or alkylmagnesium chloride, preferably those having an alkyl group of 1~ 10 carbons; alkoxymagnesium chlorides, preferably those having 1 ~ 10 carbons; and aryloxymagnesium chlorides, preferably those having 6 ~ 20 carbons. The magnesium solution used in the present invention is made by dissolving the aforementioned compounds with alcohol as a solvent in the presence or absence of a hydrocarbon solvent.

As to the types of hydrocarbon solvents used in the present invention, they include aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, and kerosene; alicyclic hydrocarbons such as cyclobenzene, methylcyclobenzene, cyclohexane, and methylcyclohexane; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, cumene, and cymene; and halogenated hydrocarbons such as dichloropropane, dichloroethylene, trichloroethylene, carbon tetrachloride, and chlorobenzene.

When a magnesium compound is converted into a magnesium solution, alcohol is used in the presence or absence of the aforementioned hydrocarbons. The types of alcohol include those containing 1 ~ 20 carbon atoms such as methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, decanol, dodecanol, octadecyl alcohol, benzyl alcohol, phenylethyl alcohol, isopropyl benzyl alcohol, and cumyl-alcohol, although alcohols containing 1 ~ 12 carbon atoms are preferable. The average size of a target catalyst and its particle distribution can vary according to the type of alcohol, the total contents, types of magnesium compounds, and the ratio of magnesium to alcohol, etc. Nevertheless, the total amount of alcohol required to obtain the magnesium solution is at least 0.5 mol per each mole of the magnesium compound, preferably about 1.0 ~ 20 mol, or more preferably about 2.0 ~ 10 mol.

The reaction of a magnesium compound with alcohol for producing magnesium solution is preferably carried out in the presence of hydrocarbon. The reaction temperature, while variable depending on the type and the amount of alcohol, is at least -25℃, preferably -10 ~ 200℃, or more preferably about 0 ~ 150℃. It is preferable to carry out the reaction for about 15 minutes ~ 5 hours, preferably for about 30 minutes ~ 4 hours.

Of the electron donors used in the present invention, the ester compounds containing at least one hydroxy group include unsaturated aliphatic acid esters having at least one hydroxy group such as 2-hydroxy ethylacrylate, 2-hydroxy ethylmethacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropylmethacrylate, 4-hydroxy butylacrylate, pentaerithritol triacrylate; aliphatic monoesters or polyesters containing at least one hydroxy group such as 2-hydroxy ethyl acetate, methyl 3-hydroxy butylate, ethyl 3-hydroxy butylate, methyl 2-hydroxy isobutylate, ethyl 2-hydroxy isobutylate, methyl 3-hydroxy-2-methyl propionate, 2,2-dimethyl-3-hydroxy propionate, ethyl-6-hydroxy hexanoate, t-butyl-2-hydroxy isobutylate, diethyl-3-hydroxy glutarate, ethyl lactate, isopropyl lactate, butyl isobutyl lactate, isobutyl lactate, ethyl mandelate, dimethyl ethyl tartrate, ethyl tartrate, dibutyl tartrate, diethyl citrate, triethyl citrate, ethyl-2-hydroxy-caproate, diethyl bis-(hydroxy methyl)malonate; aromatic esters having at least one hydroxy group such as 2-hydroxy ethyl benzoate, 2-hydroxy ethyl salicylate, methyl-4-(hydroxy methyl) benzoate, methyl-4-hydroxy benzoate, ethyl-3-hydroxy benzoate, 4-methyl salicylate, ethyl salicylate, phenyl salicylate, propyl-4-hydroxy benzoate, phenyl-3-hydroxy naphthanoate, monoethylene glycol monobenzoate, diethylene glycol benzoate, triethylene glycol benzoate; alicyclic esters having at least one hydroxy group such as lactone, and others. The amount of the ester compound containing at least one hydroxy group should be 0.001 ~ 5 mol per mole of magnesium, or preferably 0.01 ~ 2 mol per mole of magnesium.

For the silicon compound containing an alkoxy group, the other electron donor in the present invention, a compound having a general formula of $R^1_nSi(OR^2)_{4-n}$ (here, R^1 and R^2 represent a hydrocarbon having 1 ~ 12 carbons, and n for an integer of 0 ~ 3) is preferable. More specifically, it includes dimethyldimethoxy silane, dimethyldiethoxy silane, diphenyldimethoxy silane, methylphenyldimethoxy silane, diphenyldiethoxy silane, ethyltrimethoxy silane, vinyltrimethoxy silane, methyltrimethoxy silane, phenyltrimethoxy silane, methyltriethoxy silane, ethyltriethoxy silane, vinyltriethoxy silane, butyltriethoxy silane,

phenyltriethoxy silane, ethyltriisopropoxy silane, vinyltributoxy silane, ethyl silicate, butyl silicate, methyltriaryloxy silane, etc. The amount of such compound should be 0.05 ~ 3 mol per mole of magnesium, or more preferably 0.1 ~ 2 mol per mole of magnesium.

As for the temperature for the contact-reaction of a magnesium solution, an ester compound containing at least one hydroxy group, and an alkoxy silicon compound, the temperature of 0 ~ 100℃ is appropriate, or more preferably 10 ~ 70℃.

In the process, the catalyst particles are recrystallized by reacting the magnesium compound solution with a mixture of a liquid titanium compound of a general formula of $Ti(OR)_aX_{4-a}$ (R stands for an alkyl group with 1 ~ 10 carbons; X for a halogen atom; and "a" for a natural number of 0 to 4) and a silicon compound of a general formula of R_nSiCl_{4-n} (here R stands for hydrogen; or an alkyl, alkoxy, haloalkyl, or an aryl group having 1 to 10 carbons; or a halosilyl or halosilyl alkyl group having 1 to 8 carbons; n = 0-3). The types of titanium compounds which satisfy the general formula of $Ti(OR)_aX_{4-a}$ include 4-halogenated titanium such as $TiCl_4$, $TiBr_4$, and TiI_4; 3-halogenated alkoxy-titanium such as $Ti(OCH_3)Cl_3$, $Ti(OC_2H_5)Cl_3$, $Ti(OC_2H_5)Br_3$, and $Ti(O(i\text{-}C_4H_9))Br_3$; 2-halogenated alkoxy-titanium compounds such as $Ti(OCH_3)_2Cl_2$, $Ti(OC_2H_5)_2Cl_2$, $Ti(O(i\text{-}C_4H_9))_2Cl_2$, and $Ti(OC_2H_5)_2Br_2$; and tetra-alkoxy titaniums such as $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$, and $Ti(OC_4H_9)_4$. A mixture of the above titanium compounds can also be used in the present invention. However, the preferable titanium compounds are those containing halogen, or more preferably titanium tetrachloride.

The types of silicon compounds satisfying the above general formula of R_nSiCl_{4-n} include silicon tetrachloride; trichlorosilanes such as trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane; dichlorosilanes such as dimethylchlorosilane, diethyldichlorosilane, di-phenyldichlorosilane, and methylphenyldichlorosilane; monochlorosilanes such as trimethylchlorosilane; and a mixture of these silicon compounds can also be used in the present invention, or more preferably silicon tetrachloride can be used.

The amount of the mixture of a titanium compound and a silicon compound used during the re-crystallization of the magnesium compound solution is appropriately 0.1 ~ 200 mol per mole of the halogenated magnesium compound, preferably 0.1 ~ 100 mol, or more preferably 0.2

~ 80 mol. The molar ratio of a titanium compound to a silicon compound in the mixture is appropriately 0.05 ~ 0.95, or more preferably 0.1 ~ 0.8. When the magnesium compound solution is reacted with the mixture of a titanium compound and a silicon compound, the shape and the size of the resultant re-crystallized solid constituents vary a great deal according to the reaction conditions. In order to obtain the target size of the catalyst, and the target bulk density of the polymers, as intended by the present invention, it is advantageous to maintain the above mixture amounts for said titanium and silicon compounds, as well as their mix ratios. If it is outside of the above range, it will be difficult to obtain the results as intended. The reaction of the magnesium compound with the mixture of a titanium compound and a silicon compound should be carried out preferably at a sufficiently low temperature to result in formation of solid constituents. More preferably, the reaction should be carried out by contact-reaction at -70 ~ 70℃, or most preferably at -50 ~ 50℃. After the contact-reaction, the reacting temperature is slowly raised for sufficient reaction for the duration of 0.5 ~ 5 hours at 50 ~ 150℃.

The particles of the solid catalysts obtained during the above process can be further reacted with titanium compounds. These titanium compounds are titanium halides, and halogenated alkoxy titanium with an alkoxy functional group of 1 ~ 20 carbons. At times, a mixture of these compounds can also be used. Of these compounds, however, titanium halide and a halogenated alkoxy titanium compound having an alkoxy functional group of 1~8 carbons can be appropriately used, or more preferably titanium tetrahalide can be used.

Further, the solid complex titanium catalysts produced during the process of the present invention can be utilized during homo-polymerization or co-polymerization of ethylene. In particular, the catalyst is used in homo-polymerization of ethylene, and also in co-polymerization of ethylene and α-olefin such as propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, or 1-hexene having three or more carbons.

The polymerization reaction in the presence of the catalyst of the present invention is carried out by means of using (i) a solid complex titanium catalyst of the present invention, comprising magnesium, titanium, halogen, and electron donors, and (ii) a cocatalyst comprising compounds of organic metals of Groups II and III of the Periodic Table.

The solid complex titanium catalyst constituents of the present invention can be used in pre-polymerization of ethylene or α-olefin prior to the use in the aforementioned polymerization reaction. The pre-polymerization can be carried out in the presence of a hydrocarbon solvent such as hexane, at a sufficiently low temperature, with ethylene or α-olefin under pressure, in the presence of the above catalyst constituents and such an organic aluminum compound as triethylaluminum. Pre-polymerization, by maintaining the shape of the catalyst by surrounding the catalyst particles with polymers, is helpful in producing good-quality post-polymerization shape of the polymers. The weight ratio of the polymers to the catalysts after pre-polymerization is ordinarily 0.1 : 1 to 20 : 1.

The organometallic compound in the present invention can be represented by a general formula of MR_n, wherein, M stands for a metal constituent of Group II or IIIA in the Periodic Table, such as magnesium, calcium, zinc, boron, aluminum, and gallium, R for an alkyl group with 1 ~ 20 carbons, such as a methyl, ethyl, butyl, hexyl, octyl, or decyl group, and n for the atomic value of the metal constituent. As for more preferable organometallic compounds, trialkyl aluminum having an alkyl group of 1 ~ 6 carbons, such as triethylaluminum and triisobutylaluminum, or the mixture thereof can be utilized. On occasions, an organic aluminum compound having one or more halogen or hydride groups, such as ethylaluminum dichloride, diethylaluminum chloride, ethyl-aluminum sesqui-chloride, or diisobutylaluminum hydride can also be used.

As for the polymerization reaction, it is possible to carry out either gas phase or bulk polymerization in the absence of an organic solvent, or liquid slurry polymerization in the presence of an organic solvent. These polymerization methods, however, are carried out in the absence of oxygen, water, or other compounds that may act as catalytic poison.

The concentration of the solid complex titanium compound (i) with respect to the polymerization system, in the case of a liquid phase slurry polymerization, is approximately 0.001 ~ 5 mmol in terms of the titanium atom of the catalyst per one liter of the solvent, or more preferably approximately 0.001 ~ 0.5 mmol. As for the solvent, the following compounds or the mixtures thereof can be used: alkanes or cycloalkanes such as pentane, hexane, heptane, n-

octane, isooctane, cyclohexane, methylcyclohexane; alkylaromatic such as toluene, xylene, ethylbenzene, isopropylbenzene, ethyltoluene, n-propylbenzene, diethylbenzene; and halogenated aromatics such as chlorobenzene, chloronaphthalene, ortho-dichlorobenzene.

In the case of gas phase polymerization, the amount of the solid complex titanium catalyst (i) should be approximately 0.001 ~ 5 mmol in terms of the titanium atom of the catalyst per one liter of the polymerization reactant, preferably approximately 0.001 ~ 1.0 mmol, or more preferably approximately 0.01 ~ 0.5 mmol.

The preferable concentration of the organometallic compound (ii) is about 1 ~ 2,000 mol, as calculated by the aluminum atoms, per mole of the titanium atoms in the catalyst (i), or more preferably about 5 ~ 500 mol.

To secure a high reaction rate of polymerization, the polymerization herein is carried out at a sufficiently high temperature, regardless of the polymerization manufacturing process. Generally, the temperature of approximately 20 ~ 200℃ is appropriate, or more preferably approximately 20 ~ 95℃. The appropriate pressure of monomers at the time of polymerization is the atmospheric to 100 atm, or more preferably 2 ~ 50 atm.

In the present invention, in order to evaluate the hydrogen reactivity of the catalyst, the changes in the molecular weight according to the amount of hydrogen at the time of polymerization are shown as a melt index (ASTM D 1238), the index generally known in the art. The value of the melt index generally becomes greater as the molecular weight decreases.

The products obtained by the method of polymerization of the present invention are solid ethylene homogeneous polymers or the copolymers of ethylene and α-olefin, which have excellent bulk density and fluidity. Since the polymer yields are sufficiently high, there is no need for the removal of the catalyst residues.

The present invention is further described by means of the examples and comparative examples as below but should not be confined or limited to these examples.

Example 1

Production of catalyst

A solid complex titanium catalyst was produced by means of the following three steps:

(i) Step : Production of magnesium solution

Into a 1.0L reactor equipped with a mechanical stirrer, replaced with nitrogen atmosphere, 9.5 g (0.1 mol) of $MgCl_2$ and 400 ml of toluene were placed therein. After they were stirred at 300 rpm, 62 ml (0.4 mol) of 2-ethyl hexanol was added thereto. The temperature was raised to 120℃, and then the reaction was allowed to continue for three hours. The homogenous solution, which was obtained after the reaction, was cooled to 70℃.

(ii) Step : Contact-reaction of a magnesium solution, an ester containing a hydroxy group and an alkoxy silane compound

To the magnesium solution, cooled to 70℃ as above, 1.2 ml (10 mmol) of 2-hydroxyethyl methacrylate and 10.0 ml (45 mmol) of silicon tetraethoxide were added, and then the reaction was allowed to continue for an hour.

(iii) Step : Treatment of a mixture of a titanium compound and a silicon compound

After cooling the above solution to room temperature (25℃), a solution mixture of 30 ml of titanium tetrachloride and 30 ml of silicon tetrachloride was dripped into the above solution for one hour. After the completion of the dripping process, the temperature of the reactor was raised to 90℃ while stirring, after which was maintained at that temperature for one hour. After stopping the stirring, the supernatant of the solution was removed, and to the remaining solid layer was added 300 ml of toluene and 100 ml of titanium tetrachloride in sequence. There, the temperature was raised to 100℃ and

maintained thereat for two hours. After the reaction, the reactor was cooled to room temperature and the washing of the resulting solid product with 400ml of hexane was repeated until the removal of the unreacted titanium chloride. The titanium content of the solid catalyst so produced was 3.6 %.

Polymerization

A 2-L high-pressure reactor was dried in an oven and assembled while still hot. In order to make the inside of the reactor nitrogen atmosphere, nitrogen and vacuum were alternatively manipulated three times in the reactor. To the reactor was added 1,000 ml of n-hexane, after which 2 mmols of triethylaluminum and a solid catalyst by 0.03 mmol in terms of the titanium atoms were added thereto. Then, 2000 ml of hydrogen was added. The temperature was raised to 80℃ while stirring at 700 rpm. The pressure of ethylene was adjusted to 80 psi, and the polymerization was allowed to continue for an hour. After the polymerization, the temperature of the reactor was lowered to room temperature, and a large amount of ethanol was added to stop the polymerization. The polymer thus produced was collected by separation and was dried in an oven at 50℃ for at least six hours, whereby polyethylene was obtained in the form of white powder.

The polymerization activity (kg of polyethylene divided by mmol of Ti) was calculated as the weight (kg) ratio of the polymers as produced per the amount of the catalysts so used (mmol of Ti). The results of the polymerization are shown in Table 1, together with the bulk density (g/ ml) of the polymers and the melt index (g/10 minutes).

Example 2

The catalyst was prepared the same as in Example 1, except that in Step (ii) of Example 1, the temperature of the magnesium solution was adjusted to room temperature (25℃). The titanium content of the catalyst thus produced was 3.2 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 3

The catalyst was prepared the same as in Example 2, except that in Step (ii) of Example 2, 2.4 ml of 2-hydroxyethyl methacrylate and 10.0 ml of silicon tetraethoxide were used. The titanium content of the catalyst thus produced was 2.9 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 4

The catalyst was prepared the same as in Example 2, except that in Step (ii) of Example 2, 3.6 ml of 2-hydroxyethyl methacrylate and 10.0 ml of silicon tetraethoxide were used. The titanium content of the catalyst thus produced was 2.5 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 5

The catalyst was prepared the same as in Example 2, except that in Step (ii) of Example 2, 1.2 ml of 2-hydroxyethyl methacrylate and 5.0 ml of silicon tetraethoxide were used for the production of the catalyst. The titanium content of the catalyst thus produced was 3.5 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 6

The catalyst was prepared the same as in Example 2, except that in Step (ii) of Example 2, 1.2 ml of 2-hydroxyethyl methacrylate and 15.0 ml of silicon tetraethoxide were used for the production of the catalyst. The titanium content of the catalyst thus produced was 3.1 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 7

The catalyst was prepared the same as in Example 2, except that in Step (iii) of Example 2, 30 ml of titanium tetrachloride and 30 ml of silicon tetrachloride were dripped in the period of 30 minutes for the production of the catalyst. The titanium content of the catalyst thus produced

was 3.8 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 8

The catalyst was prepared the same as in Example 2, except that in Step (iii) of Example 2, 30 ml of titanium tetrachloride and 30 ml of silicon tetrachloride were dripped in the period of 2 hours for the production of the catalyst. The titanium content of the catalyst thus produced was 3.6 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 9

The polymerization was carried out using the catalyst produced in Example 1 and 1500 ml of hydrogen, and the results thereof are shown in Table1.

Example 10

The polymerization was carried out using the catalyst produced in Example 1 and 1000 ml of hydrogen, and the results thereof are shown in Table1.

Example 11

The catalyst was prepared the same as in Example 2, except that in Step (i) in Example 2, 400 ml of decane was used in the production of magnesium solution. The titanium content of the catalyst thus produced was 3.6 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 12

The catalyst was prepared the same as in Example 11, except that in Step (iii) of Example 11, 40 ml of titanium tetrachloride and 20 ml of silicon tetrachloride were used. The titanium

content of the catalyst thus produced was 3.8 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 13

The catalyst was prepared the same as in Example 12, except that in Step (iii) of Example 12, 20 ml of titanium tetrachloride and 40 ml of silicon tetrachloride were used. The titanium content of the catalyst thus produced was 3.4 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 14

The catalyst was prepared the same as in Example 2, except that in Step (iii) of Example 2, 40 ml of titanium tetrachloride and 20 ml of silicon tetrachloride were used. The titanium content of the catalyst thus produced was 3.9 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 15

The catalyst was prepared the same as in Example 2, except that in Step (iii) of Example 2, 20 ml of titanium tetrachloride and 40 ml of silicon tetrachloride were used. The titanium content of the catalyst thus produced was 3.5 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Comparative Example 1

The catalyst was prepared the same as in Example 2, except that in Step (ii) of Example 2, 10.0 ml of silicon tetraethoxide was added and 2-hydroxyethyl methacrylate was not used. The titanium content of the catalyst thus produced was 3.8 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Comparative Example 2

The catalyst was prepared the same as in Example 2, except that in Step (ii) of Example 2, 1.2 ml of 2-hydroxyethyl methacrylate was added and silicon tetraethoxide was not used. The titanium content of the catalyst thus produced was 3.4 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Comparative Example 3

The catalyst was prepared the same as in Example 2, except that in Step (ii) of Example 2, neither 2-hydroxyethyl methacrylate nor silicon tetraethoxide was used. The titanium content of the catalyst thus produced was 4.3 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Comparative Example 4

The catalyst was prepared the same as in Example 2, except that in Step (iii) of Example 2, 60 ml of titanium tetrachloride was used. The titanium content of the catalyst thus produced was 4.4 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Comparative Example 5

The polymerization was carried out using the catalyst produced in Comparative Example 4 and 1500 ml of hydrogen. The results thereof are shown in Table 1.

Comparative Example 6

The polymerization was carried out using the catalyst produced in Comparative Example 4 and 1000 ml of hydrogen. The results thereof are shown in Table 1.

Comparative Example 7

The catalyst was prepared the same as in Example 2, except that in Step (ii) of Example 2, neither 2-hydroxyethyl methacrylate nor silicon tetraethoxide was used, and in Step (iii), 60 ml of titanium tetrachloride was used. The titanium content of the catalyst thus produced was 4.1 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Table 1 Results of Polymerization

Example	Amount of Hydrogen (ml)	Activity (kg PE/mmol Ti)	Bulk Density (g/ml)	Melting Index (g/10min)
1	2,000	2.3	0.36	38.9
2	2,000	2.1	0.35	35.2
3	2,000	2.5	0.34	38.4
4	2,000	2.3	0.33	39.2
5	2,000	2.6	0.34	33.1
6	2,000	2.0	0.36	32.4
7	2,000	2.7	0.32	38.1
8	2,000	2.1	0.35	34.8
9	1,500	2.8	0.34	19.8
10	1,000	3.9	0.32	3.8
11	2,000	2.2	0.34	36.4
12	2,000	2.4	0.35	31.7
13	2,000	2.0	0.33	34.8
14	2,000	2.6	0.36	38.9
15	2,000	2.4	0.35	36.8
CE1	2,000	1.4	0.35	12.4
CE2	2,000	1.6	0.32	22.6
CE3	2,000	1.2	0.28	8.2
CE4	2,000	2.2	0.32	18.1
CE5	1,500	2.9	0.32	7.8
CE6	1,000	3.6	0.31	2.7
CE7	2,000	1.1	0.22	7.8

* CE : Comparative Example

As shown above, the production process of the catalyst of the present invention for homo-polymerization and co-polymerization of ethylene is simple with excellent catalytic activity. Further, with the catalyst particles being controlled, high bulk density of the polymer can be provided, and the hydrogen sensitivity is greatly improved.

Claims

What is claimed is:

1. A solid titanium catalyst for homo-polymerization and co-polymerization of ethylene, wherein said catalyst is produced by:

(i) preparing a magnesium compound solution by contacting a halogenated magnesium compound with alcohol;

(ii) reacting said solution with an ester compound having at least one hydroxy group and a silicon compound having an alkoxy group; and

(iii) reacting said solution from above(ii) with a mixture of a titanium compound and a silicon compound to produce solid catalyst, and optionally the solid catalyst are further reacted with a titanium compound.

2. A solid titanium catalyst according to Claim 1, wherein said ester compound having at least one hydroxy group is an unsaturated aliphatic acid ester having at least one hydroxy group, which is selected from the group consisting of 2-hydroxy ethylacrylate, 2-hydroxy ethylmethacrylate, 2-hydroxy propyl acrylate, 2-hydroxy propylmethacrylate, 4-hydroxy butylacrylate, pentaerithritol triacrylate; an aliphatic monoester or polyester having at least one hydroxy group, which is selected from the group consisting of 2-hydroxy ethyl acetate, methyl 3-hydroxy butylate, ethyl 3-hydroxy butylate, methyl 2-hydroxy isobutylate, ethyl 2-hydroxy isobutylate, methyl 3-hydroxy-2-methyl propionate, 2,2-dimethyl-3-hydroxy propionate, ethyl-6-hydroxy hexanoate, t-butyl-2-hydroxy isobutylate, diethyl-3-hydroxy glutarate, ethyllactate, isopropyl lactate, butyl-isobutyl lactate, isobutyl lactate, ethyl mandelate, dimethyl ethyl tartrate, ethyl tartrate, dibutyl tartrate, diethyl citrate, triethyl citrate, ethyl-2-hydroxy-caproate, diethyl *bis*-(hydroxymethyl) malonate; an aromatic ester having at least one hydroxy group, which is selected from the group consisting of 2-hydroxy ethyl benzoate, 2-hydroxy ethyl salicylate, methyl-4-(hydroxy methyl) benzoate, methyl-4-hydroxy benzoate, ethyl-3-hydroxy benzoate, 4-methyl salicylate, ethyl salicylate, phenyl salicylate, propyl-4-hydroxy benzoate, phenyl-3-hydroxy naphthanoate, monoethylene glycol

monobenzoate, diethylene glycol benzoate, triethylene glycol monobenzoate; and an alicyclic ester having at least one hydroxy group as in hydroxy butyl-lactone; and wherein said silicon compound having an alkoxy group is represented by the general formula of $R^1_nSi(OR^2)_{4-n}$, where R^1 and R^2 represent a hydrocarbon having 1 ~ 12 carbons, and n for an integer of 0 ~ 3, said silicon compound being selected from the group consisting of dimethyldimethoxy silane, dimethyldiethoxy silane, diphenyldimethoxy silane, methylphenyldimethoxy silane, diphenyldiethoxy silane, ethyltrimethoxy silane, vinyltrimethoxy silane, methyltrimethoxy silane, phenyltrimethoxy silane, methyltriethoxy silane, ethyltriethoxy silane, vinyltriethoxy silane, butyltriethoxy silane, phenyltriethoxy silane, ethyltriisopropoxy silane, vinyltributoxy silane, ethylsilicate, butylsilicate, and methyltriaryloxy silane.

3. A solid titanium catalyst according to Claim 1, wherein said titanium compound is represented by the general formula of $Ti(OR)_aX_{4-a}$, where R stands for an alkyl group with 1 ~ 10 carbons, X for a halogen atom, and "a" for an integer of 0 to 4; and wherein said silicon compound is represented by the general formula of R_nSiCl_{4-n}, where R stands for hydrogen, or an alkyl, alkoxy, haloalkyl, or aryl group having 1 to 10 carbons; or a halosilyl or halosilyl alkyl group having 1 to 8 carbons; n = an interger of 0 to 4.

4. A solid titanium catalyst according to Claim 3, wherein said titanium compound is a 4-halogenated titanium, which is selected from the group consisting of $TiCl_4$, $TiBr_4$, and TiI4; a 3-halogenated alkoxy titanium, which is selected from the group consisting of $Ti(OCH_3)Cl_3$, $Ti(OC_2H_5)Cl_3$, $Ti(OC_2H_5)Br_3$, and $Ti(O(i\text{-}C_4H_9))Br_3$; a 2-halogenated alkoxy titanium, which is selected from the group consisting of $Ti(OCH_3)_2Cl_2$, $Ti(OC_2H_5)_2Cl_2$, $Ti(O(i\text{-}C_4H_9))_2Cl_2$, and $Ti(OC_2H_5)_2Br_2$; and a tetralkoxy titanium, which is selected from the group consisting of $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$, and $Ti(OC_4H_9)_4$; and wherein said silicon compound is a silicon tetrachloride; a trichlorosilane such as trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, and phenyl-trichlorosilane; a dichlorosilane such as dimethylchlorosilane, diethyldichlorosilane, diphenyldichlorosilane, and methylphenyldichlorosilane; and a monochlorosilane such as trimethylchlorosilane.

5. A solid titanium catalyst according to Claim 3, wherein said titanium compound is titanium tetrachloride, and said silicon compound is silicon tetrachloride.

6. A solid titanium catalyst according to Claim 1, wherein the amount of the mixture of a titanium compound and a silicon compound is 0.1 ~ 200 mol per mole of said halogenated magnesium compound, and the molar ratio of said titanium compound to said silicon compound in the mixture is 0.05 ~ 0.95.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR99/00639

A. CLASSIFICATION OF SUBJECT MATTER

IPC^7: C 08 F 4/654, C 08 F 10/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC^7: C 08 F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, PAJ, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5459116 A (Ro et al.) 1995.10.17 The whole document	1-6
A	US 5438110 A (Ishimaru et al.) 1995.08.01 Example 3	1-6
A	EP 669347 A1 (Mitsui Petrochemical Industries, Ltd.) 1995 08.30 Comparative examples 3 & 4	1-6

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
„A" document defining the general state of the art which is not considered to be of particular relevance
„E" earlier application or patent but published on or after the international filing date
„L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
„O" document referring to an oral disclosure, use, exhibition or other means
„P" document published prior to the international filing date but later than the priority date claimed

„T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
„X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
„Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
„&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 December 1999 (06.12.99)	29 March 2000 (29.03.00)
Name and mailing address of the ISA/AT Austrian Patent Office Kohlmarkt 8-10; A-1014 Vienna Facsimile No. 1/53424/200	Authorised officer Pusterer Telephone No. 1/53424/331

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR 99/00639

Patent document cited in search report			Publication date	Patent family member(s)			Publication date
US	A	5459116	17-10-1995	CN	A	1099041	22-02-1995
				CN	B	1041097	09-12-1998
				JP	A2	7149813	13-06-1995
				JP	B2	2680262	19-11-1997
				KR	B1	123016	12-11-1997
US	A	5438110	01-08-1995	US	A	4990479	05-02-1991
				AT	E	102223	15-03-1994
				CA	A1	1338088	27-02-1996
				CN	A	1225369	11-08-1999
				DE	C0	68913375	07-04-1994
				DE	T2	68913375	01-06-1994
				EP	A2	350170	10-01-1990
				EP	A3	350170	27-03-1991
				EP	B1	350170	02-03-1994
				ES	T3	2052004	01-07-1994
				JP	A2	2229807	12-09-1990
				JP	B2	2723138	09-03-1998
				KR	B1	9202488	26-03-1992
				JP	A2	2084404	26-03-1990
				JP	B2	2723137	09-03-1998
				CN	A	1040379	14-03-1990
				CN	B	1043233	05-05-1999
EP	A1	669347	30-08-1995	CA	AA	2142753	19-08-1995
EP	B1	669347	06-05-1998	CA	C	2142753	29-09-1998
				DE	C0	69502315	10-06-1998
				DE	T2	69502315	05-11-1998
				JP	A2	7228629	29-08-1995
				KR	B1	178075	15-05-1999
				US	A	5731393	24-03-1998

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 99-PCT-009	**FOR FURTHER ACTION** See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/KR 99/00639	International filing date (*day/month/year*) 23 October 1999 (23.10.1999)	Priority Date (*day/month/year*) 27 May 1999 (27.05.1999)
International Patent Classification (IPC) or national classification and IPC IPC^7: C08F 4/654, C08F 10/02		
Applicant SAMSUNG GENERAL CHEMICALS CO., LTD. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examination Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of ________ sheets.

3. This report contains indications relating to the following items:

   I. ☒ Basis of the opinion
   II. ☐ Priority
   III. ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   IV. ☐ Lack of unity of invention
   V. ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   VI. ☐ Certain documents cited
   VII. ☐ Certain defects in the international application
   VIII. ☐ Certain observations on the international application

Date of submission of the demand 13 January 2000 (13.01.2000)	Date of completion of this report 16 January 2001 (16.01.2001)
Name and mailing address of the IPEA/AT Austrian Patent Office Kohlmarkt 8-10 A-1014 Vienna Facsimile No. 1/53424/200	Authorized officer PUSTERER Telephone No. 1/53424/311

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/KR 99/00639

I. Basis of the report

1. With regard to the **elements** of the international application:*

☒ the international application as originally filed

☐ the description:
pages ______, as originally filed
pages ______, filed with the demand
pages ______, filed with the letter of ______.

☐ the claims:
pages ______, as originally filed
pages ______, as amended (together with any statement) under Article 19
pages ______, filed with the demand
pages ______, filed with the letter of ______.

☐ the drawings:
pages ______, as originally filed
pages ______, filed with the demand
pages ______, filed with the letter of ______.

☐ the sequence listing part of the description:
pages ______, as originally filed
pages ______, filed with the demand
pages ______, filed with the letter of ______.

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language ______ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

☐ the description, pages ______.

☐ the claims, Nos. ______.

☐ the drawings, sheets/fig ______.

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

** *Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/KR 99/00639

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-6	YES
	Claims		NO
Inventive step (IS)	Claims	1-6	YES
	Claims		NO
Industrial applicability (IA)	Claims	1-6	YES
	Claims		NO

Citations and explanations (Rule 70.7)

The following documents have been considered for the purposes of this report:

D1: US 5459116 A
D2: US 5438110 A
D3: EP 669347 A1

Having regard to the cited documents D1, D2 and D3 the present application meets the criteria as defined in the regulations (Article 33 (2)-(4) PCT), because the subject-matter of the claims 1 – 6 is new and shows an inventive step with respect of the prior art also.
Additionally the claimed application can undoubtedly be industrially applied.

EO/US
PCT/KR99/00639

F ENT COOPERATION TREA

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark
Office, PCT
2011 South Clark Place Room
CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing: 07 December 2000 (07.12.00)	
International application No.: PCT/KR99/00639	Applicant's or agent's file reference: 99-PCT-009
International filing date: 23 October 1999 (23.10.99)	Priority date: 27 May 1999 (27.05.99)
Applicant: YANG, Chun, Byung	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International preliminary Examining Authority on:

13 January 2000 (13.01.00)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was
[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

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The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer: J. Zahra Telephone No.: (41-22) 338.83.38